

MESO-SUBSTITUTED ANIONIC METALLOPORPHYRIN CATALYSTS
IMMOBILIZED ON IONIC LIQUID-FUNCTIONALIZED MESOPOROUS
SILICA IN OXIDATION OF TRIMETHYLPHENOL

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Special dedicated to;

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*Roslan Othman and Asnani Asmar for their love and care, continuous prayer,
endless support and encouragement they have provided all these years for me.*

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ABSTRACT

Synthetic metalloporphyrins have been extensively studied as biomimetic models for cytochrome P-450 oxidative enzymes in catalysis of different substrates. Despite the advantages of superior activity and selectivity, as well as mild reaction temperatures, difficulties in catalyst recovery and purification of products still constitute the major drawbacks of homogeneous processes. This research aimed to develop new heterogeneous catalysts of *meso*-tetra-(4-sulfonatophenyl)porphyrinato metal complexes (MTSPP) immobilized in ionic liquid-functionalized mesoporous silica SBA-15. Hence, positively charged ionic liquid, 1-methyl-3-(3-triethoxysilylpropyl) imidazolium chloride (C_3mimCl , denoted as ImIL) was explored as an interface linker for immobilization of the anionic MTSPP complexes onto the mesoporous silica support by electrostatic interactions. A series of ImIL-functionalized SBA-15 (ImIL@SBA) materials with different loadings of ImIL (1.0–10.0 mmol) were prepared via the post-synthesis covalent grafting method. The immobilization of MTSPP complexes on the ImIL@SBA with different MTSPP loading (5, 10 and 25 μmol) was carried-out via the post-synthesis ion-exchange method to afford the MTSPP-ImIL@SBA (M: Mn, Fe, Cu and Zn) nanocomposites. The TGA results showed the relative stability of the MTSPP-ImIL@SBA catalysts decreased in the order of strength of metal ion binding: $Cu(II) > Mn(II) > Zn(II) > Fe(II)$, which correlated directly with metal core electronegativity effect. The DRUV-Vis spectroscopy confirmed that FeTSPP could form iron porphyrin μ -oxo-dimeric species upon immobilization onto the surface of mesoporous silica support, which would cause the thermal stability of FeTSPP-ImIL@SBA to become very low. The catalytic properties of MTSPP-ImIL@SBA was tested in the one-step oxidation of 2,3,6-trimethylphenol (TMP) to 2,3,5-trimethylbenzoquinone (TMBQ) as a model reaction. Factors influencing the reaction were studied systematically, and a possible reaction mechanism was then proposed. The catalytic activity trend of the MTSPP-ImIL@SBA increased in the order of metal ion: $Cu(II) > Mn(II) > Zn(II) > Fe(II)$. Under the optimum condition, CuTSPP-ImIL@SBA showed excellent performance with 80–100% conversions of TMP and 100% selectivity for TMBQ. Furthermore, MTSPP-ImIL@SBA catalysts were highly stable and reusable up to four cycles without a significant loss of activity, with a high TON value of 1302 after 24 hours and TOF up to $54\ h^{-1}$, which were readily attainable under mild reaction conditions. As a conclusion, the cationic ImIL linker in the MTSPP-ImIL@SBA seemed to play a pivotal role in the catalytic mechanism by enhancing the chemical stability of the anionic MTSPP complexes. Therefore, the MTSPP-ImIL@SBA nanocomposites emerged as potential heterogeneous catalysts for the production of TMBQ, the chemical intermediate for the industrial production of Vitamin E.

ABSTRAK

Metaloporfirin sintetik telah dikaji secara meluas sebagai model biomimetik untuk enzim oksidatif sitokrom P-450 dalam pemangkinan substrat yang berlainan. Meskipun mempunyai kelebihan seperti aktiviti dan kepilihan yang tinggi serta suhu tindak balas yang sederhana, namun pemisahan mangkin dan penulenan produk yang rumit masih merupakan kelemahan utama proses homogen. Penyelidikan ini bertujuan membangunkan mangkin heterogen baharu yang terdiri daripada kompleks logam *meso*-tetra-(4-sulfonatofenil)porfirin (MTSPP) yang dipegunkan pada silika mesoliang SBA-15 berfungsi-kecair ionik. Maka, cecair ionik bercas positif, iaitu 1-metil-3-(3-trietoksilpropil) imidazolium klorida (C_3mimCl , disimbolkan sebagai ImIL) telah diteroka sebagai pemaut antara muka untuk pemegungan kompleks anionik MTSPP kepada penyokong silika mesoliang secara kaedah interaksi elektrostatik. Siri bahan SBA-15 berfungsi-ImIL (ImIL@SBA) dengan muatan ImIL yang berbeza-beza (1.0-10.0 mmol) telah disediakan menggunakan kaedah pencangkungan kovalen pasca-sintesis. Pemegungan kompleks MTSPP pada ImIL@SBA dengan muatan MTSPP berlainan (5, 10 dan 25 μ mol) telah dijalankan melalui kaedah penukaran ion pasca-sintesis bagi menghasilkan nanokomposit MTSPP-ImIL@SBA (M: Mn, Fe, Cu dan Zn). Keputusan TGA menunjukkan bahawa kestabilan relatif mangkin MTSPP-ImIL@SBA berkurang mengikut tertib kekuatan penambatan ion logam: $Cu(II) > Mn(II) > Zn(II) > Fe(II)$, yang berkorelasi langsung dengan kesan elektronegativiti logam pusat. Spektroskopi DRUV-Vis mengesahkan bahawa FeTSPP mampu membentuk dimer μ -okso ferum porfirin ketika dipegunkan pada permukaan penyokong silika mesoliang, yang mungkin mengakibatkan kestabilan terma FeTSPP-ImIL@SBA menjadi sangat rendah. Sifat pemangkinan MTSPP-ImIL@SBA telah diuji dalam pengoksidaan satu langkah 2,3,6-trimetilfenol (TMP) kepada 2,3,5-trimetilbenzokuinon (TMBQ) sebagai model tindak balas. Faktor yang mempengaruhi tindak balas telah dikaji secara sistematik, dan mekanisme tindak balas yang munasabah kemudiannya dicadangkan. Kecenderungan aktiviti pemangkinan MTSPP-ImIL@SBA bertambah mengikut tertib ion logam: $Cu(II) > Mn(II) > Zn(II) > Fe(II)$. Dalam keadaan optimum, CuTSPP-ImIL@SBA menunjukkan prestasi yang cemerlang dengan penukaran 80-100% untuk TMP dan kepilihan 100% untuk TMBQ. Tambahan lagi, mangkin MTSPP-ImIL@SBA adalah sangat stabil dan dapat diguna semula sehingga empat kitaran tanpa kehilangan aktiviti yang signifikan, dengan TON yang tinggi bernilai 1302 selepas 24 jam dan TOF sehingga 54 h^{-1} , yang mudah tercapai pada keadaan tindak balas sederhana. Sebagai kesimpulan, pemaut ImIL kationik dalam MTSPP-ImIL@SBA kelihatan memainkan peranan penting dalam mekanisme pemangkinan dengan mempertingkatkan kestabilan kimia kompleks anionik MTSPP. Oleh kerana itu, nanokomposit MTSPP-ImIL@SBA muncul sebagai mangkin heterogen berpotensi untuk penghasilan TMBQ, bahan kimia perantaraan bagi penghasilan industri Vitamin E.

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LIST OF ABBREVIATIONS

^{13}C CP-MAS NMR	-	Carbon-13 Cross Polarization-Magic Angle Spinning Nuclear Magnetic Resonance
^1H -NMR	-	Proton Nuclear Magnetic Resonance
^{29}Si MAS NMR	-	Silicon-29 Magic Angle Spinning Nuclear Magnetic Resonance
ac-SBA-15	-	After calcination SBA-15
as-SBA-15	-	As-synthesized SBA-15
ase-SBA-15	-	After Soxhlet extraction SBA-15
BET	-	Brunauer-Emmet-Teller
BJH	-	Barret-Jouner-Halenda
C_3mimCl	-	1-Methyl-3-(3-triethoxysilylpropyl)imidazolium chloride
CDCl_3		Chloroform
CPTES	-	(3-chlororopyl)triethoxysilane
CuTSPP-ImIL@SBA	-	CuTSPP immobilized onto ImIL@SBA
CuTSPP	-	(<i>meso</i> -tetra-(4-sulfonatophenyl)porphyrinato) Cu(II)
DMSO		Dimethyl sulfoxide
DR UV-Vis	-	Diffuse Reflectance Ultraviolet-Visible
EB	-	Ethyl benzoate
EDX	-	Energy Dispersive X-Ray
FDU	-	Fudan University
FeTSPP-ImIL@SBA	-	FeTSPP immobilized onto ImIL@SBA
FeTSPP	-	(<i>meso</i> -tetra-(4-sulfonatophenyl)porphyrinato) Fe(II)
FESEM	-	Field Emission Scanning Electron Microscope

FSM	-	Folding Sheet Materials
FTIR	-	Fourier Transform Infrared Spectroscopy
GC-FID	-	Gas chromatography-flame ionization detector
GC-MS	-	Gas chromatography-mass spectrometry
H ₂ TPP	-	<i>meso</i> -tetraphenylporphyrin
H ₂ TSPP	-	<i>meso</i> -tetra-(4-sulfonatophenyl)porphyrin
HOM	-	Highly Ordered Mesoporous Silica
HMS	-	Hexagonal Mesoporous Silica
HOMO	-	Highest occupied molecular orbital
ICP-OES	-	Inductively Coupled Plasma-Optical Emission Spectroscopy
IL	-	Ionic liquid
ImIL	-	Ionic liquid C ₃ mimCl
ImIL@SBA	-	ImIL-functionalized SBA-15
KIT	-	Korean Institute of Science and Technology
LUMO	-	Lowest unoccupied molecular orbital
MALDI-TOF MS	-	Matrix Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry
MCM	-	Mobil Composition Matter
MTSPP	-	Metalloporphyrin Complexes of H ₂ TSPP
MTSPP-ImIL@SBA	-	MTSPP complexes immobilized onto ImIL@SBA
MnTSPP	-	(<i>meso</i> -tetra-(4-sulfonatophenyl)porphyrinato) Mn(II)
MnTSPP-ImIL@SBA	-	MnTSPP immobilized onto ImIL@SBA
MSU	-	Michigan State University
Pluronic P123	-	(Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) copolymer
SBA	-	Santa Barbara Amorphous
SAXS	-	Small Angle X-Ray Scattering
TBHP	-	<i>tert</i> -butyl hydroperoxide
TEM	-	Transmission Electron Microscopy
TEOS	-	Tetraethyl orthosilicate

TGA	-	Thermogravimetric analysis
TMP	-	2,3,6-Trimethylphenol
TMBQ	-	2,3,5-Trimethylbenzoquinone
TOF	-	Turnover frequency
TON	-	Turnover number
UV-Vis	-	Ultraviolet-Visible
ZnTSPP	-	(<i>meso</i> -tetra-(4-sulfonatophenyl)porphyrinato) Zn(II)
ZnTSPP-ImIL@SBA	-	ZnTSPP immobilized onto ImIL@SBA

LIST OF SYMBOLS

A	-	Absorbance
a_o	-	Unit cell parameter
d_{100}	-	d-spacing at (1 1 0) lattice
D_{BJH}	-	Pore diameter based on BJH model
2θ	-	Bragg angle
δ	-	Chemical shift
Da	-	Daltons
J	-	Coupling constant
Hz	-	Hertz
λ	-	Wavelength
nm	-	Nanometer
q	-	Scattering vector
Si-OH	-	Silanol
S_{BET}	-	Total specific surface area
S_{Meso}	-	Mesoporous surface area
S_{Micro}	-	Microporous surface area
V_{Total}	-	Total pore volume
V_{Meso}	-	Pore volume of mesopore
V_{Micro}	-	Pore volume of micropore
W	-	Pore wall thickness

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CHAPTER 1

INTRODUCTION

1.1 Research Background

In the past few years, there have been some rapid developments of metalloporphyrin systems which mimic the Cytochrome P-450 enzymes. Cytochrome P-450, a member of the monooxygenase family of heme enzymes, have an iron protoporphyrin IX as the prosthetic group that acts as a catalytic intermediate in several oxygenations of organic substrates (Nakagaki *et al.*, 2014; Nakagaki *et al.*, 2013; Bolzon *et al.*, 2013; Palaretti *et al.*, 2012). Furthermore, there are a large number of published studies (Barona-Castaño *et al.*, 2016; Notonier *et al.*, 2016; Krest *et al.*, 2013) that describe the application of Cytochrome P-450 as catalyst in different chemical processes, including alkene epoxidation, *n*-dealkylation of secondary and tertiary amines, *o*-dealkylation, and hydroxylation of aromatic compounds and oxidations of amines, sulfides, alcohols and aldehydes.

Recently, a considerable amount of literature has been published on synthetic metalloporphyrins with transition metals such as iron, manganese and ruthenium rhodium, cobalt, nickel, copper and zinc (Huang *et al.*, 2017; Castro *et al.*, 2017; Lü *et al.*, 2017; Carrie *et al.*, 2016; Silva Martins *et al.*, 2016; Tabor *et al.*, 2016; Barbosa *et al.*, 2016; Chan *et al.*, 2015). Besides, the studies demonstrated the metalloporphyrins as useful biomimetic catalysts for various oxidation reactions (Zhao *et al.*, 2017; Zhou *et al.*, 2016; Santos da Silva *et al.*, 2014; Rayati *et al.*, 2013). Biomimetic catalysts are known to have several advantages such as high activity, selectivity, efficiency and turnover catalytic system under mild reaction

conditions (Hajian *et al.*, 2016; Jondi *et al.*, 2016; Che and Huang, 2009). Despite its many advantages and wide range of applications, the metalloporphyrin does present certain drawbacks such as the low solubility in organic solvents. This major problem is due to the relatively high energy of their molecular lattice and their moderate energies of solvation with the low polarity chemical bonding of the macrocycle (Mamardashvili *et al.*, 2000). In addition, the use of metalloporphyrins as homogeneous catalysts have some drawbacks such as thermal decomposition during the reaction and difficulty of recovery after the reaction (Kolahdoozan *et al.*, 2013).

It has been reported that heterogenization of homogeneous catalysts is a technique that involves the immobilization of homogeneous catalysts on inorganic solid materials (Bolzon *et al.*, 2013). To date, a variety of methods have been developed and introduced to support the metalloporphyrins. Immobilization of metalloporphyrins or active metal species onto imidazolium-based IL grafted silica has been employed as an alternative method to combine the advantages of ILs (non-volatility, immiscible with non-polar solvent, good thermal stability, low vapour pressure and simple functionality) with those of metalloporphyrins. This concept of catalyst system can be achieved in many different approaches, such as simple impregnation, coordination, electrostatic interactions, covalent binding or grafting, polymerization sol-gel and encapsulation or pore trapping techniques (Rostamnia *et al.*, 2016a; Bolzon *et al.*, 2013; Gustafsson *et al.*, 2012; Nohair *et al.*, 2008; Beakley *et al.*, 2005).

One of the favoured approaches that can be used is electrostatic interactions between an ionic metalloporphyrins and counter ionic groups on the surface of silica. In other words, electrostatic interaction involves the opposite charges. Even though this method is limited only to ionic metalloporphyrins, it has been reported that the leaching of metal complexes from the support during the reactions was avoided due to the existence of strong ionic interaction (Hajian *et al.*, 2016; Gandini *et al.*, 2008; Zhao *et al.*, 2006). Imidazolium-based IL could be functionalized onto the surface of silica supports via a chemical covalent grafting method which is used as the cation in the formation of the ionic group. Therefore, in this research, imidazolium-based IL is

covalently bonded to the silica and then act as the linkers between silica and the anionic metalloporphyrins.

Many recent studies have demonstrated the use of mesoporous silica materials, in particular, SBA-15 as inorganic solid support due to their characteristic textural properties, such as a large specific surface area and pore volume, high ordered channel structures with narrow and uniform pore diameter between 3 and 30 nm (Rostamnia *et al.*, 2016b; Lei *et al.*, 2015; Rostamnia *et al.*, 2014; Xiong *et al.*, 2014). In addition, the SBA-15 silica displays dense silanol (Si–OH) groups on the surface which can readily be reacted for organic functionalization. Owing to the favourable physicochemical properties, SBA-15 had been chosen as suitable supports for the immobilization of metalloporphyrins.

Catalytic oxidation is one of the widely used processes in the chemical production of many commercial compounds (Xu *et al.*, 2015; Ali *et al.*, 2014; Guo *et al.*, 2014). In this regard, the selective oxidation of phenols to the desired quinones has been a great interest in organic synthesis. Quinones are used as intermediate in the synthesis of fine chemicals and pharmaceuticals such as perfume aromas, vitamins and drugs (Saux *et al.*, 2013; Çimen and Türk, 2008). Previous studies revealed that compounds having a benzoquinone structure displayed biologically important properties such as cardiovascular, antibacterial, antigerminative, antitumor and antiprotozoan activities (Palacio *et al.*, 2012; Li *et al.*, 2009). On the other hand, Vitamin E is the one of the most important fat-soluble biological antioxidant that has been used in food, medical treatments and cosmetics (Gao *et al.*, 2017; Kholdeeva *et al.*, 2009). Notably, the precursor in the synthesis of Vitamin E is, 2,3,5-trimethylbenzoquinone (TMBQ) which is currently produced in the industry via oxidation of 2,3,6-trimethylphenol (TMP).

So far, however, the conventional method for producing TMBQ is the oxidation of sulfonated TMP using oxidant MnO₂ which brings a large amount of waste by-products (Wang *et al.*, 2009; Guan *et al.*, 2008; Sun *et al.*, 2005). Therefore, an environmentally friendly catalytic method based on the one-step oxidation of TMP to TMBQ has been established using hydrogen peroxide or *tert*-

butyl hydroperoxide (TBHP) as “clean” oxidants (Saux *et al.*, 2013; Çimen and Türk, 2008).

Generally, the use of solid heterogeneous catalysts in liquid phase oxidation reactions is considered as a promising alternative that offer several advantages such as ease of product separation, easy catalyst recycling, easier to prepare and handle, enhance the catalytic efficiency and selectivity as well as to minimize the side product of reactions (Zanardi *et al.*, 2016; Choi *et al.*, 2015; Kolahdoozan *et al.*, 2013; Pires *et al.*, 2009; Zois *et al.*, 2007). In the past, copper halides or other copper salts, cobalt complexes with Schiff bases, ruthenium salts and heteropoly acids have been extensively reported as catalysts for the oxidation of TMP (Wang *et al.*, 2009; Li *et al.*, 2009; Guan *et al.*, 2008; Çimen and Türk, 2008; Sun *et al.*, 2005). Nevertheless, the homogeneous catalysts as mentioned above posed significant drawbacks that related to the separation, recycling and purification of products (Gao *et al.*, 2017; Kholdeeva *et al.*, 2009). To address these issues, the development of more efficient heterogeneous catalysts for such oxidation reactions is highly desired.

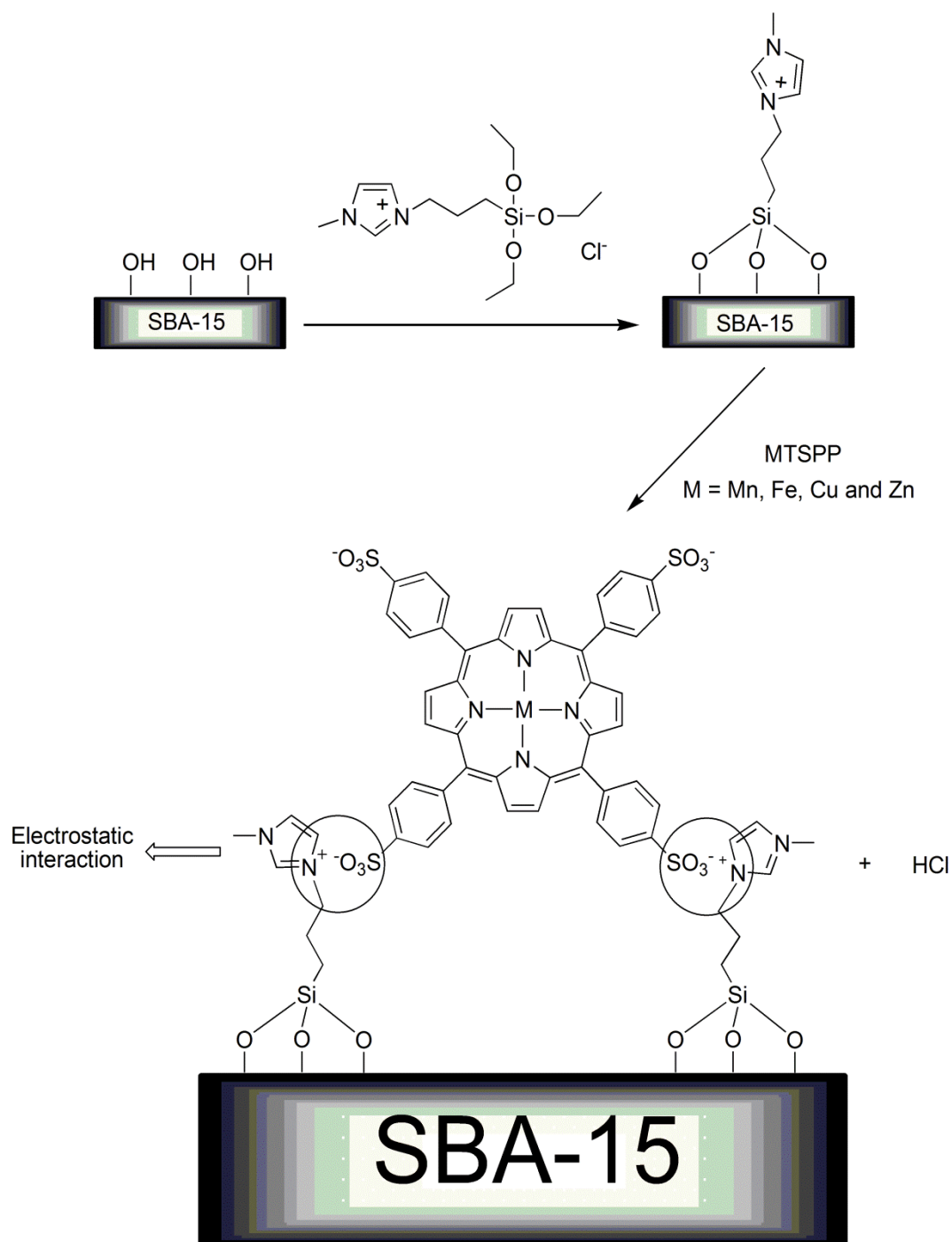
1.2 Problem Statement

One of the most attractive and significant transformation in organic reactions is oxidation of TMP to TMBQ. The TMBQ represents a key intermediate in the industrial production of vitamin E (α -tocopherol) (Möller *et al.*, 2011; Palacio *et al.*, 2012). Traditionally, TMBQ production in the industry involves two different steps; *para*-sulfonation of TMP, and chemical oxidation with an inorganic oxidizing agent such as manganese oxide (MnO_2). Still, the major problems associated with this approach are the high capital cost and the safe disposal of solids and liquid wastes, due to high consumption of sulfuric acid and the use of stoichiometric amounts of solid oxidants, and reductants (Çimen and Türk, 2008).

An alternative one-step oxidation of TMP to TMBQ has been demonstrated using several homogeneous transition-metal-based catalysts such as cobalt

complexes with Schiff bases, copper complexes, Fenton's reagent, hetero-polyacids, iron halides and metallophthalocyanines with clean oxidizing agents (Li *et al.*, 2009; Li and Liu, 2004; Sorokin and Tuel, 2000). Nevertheless, the low conversion of TMP was mainly due to the poor selectivity, recovery and deactivation of the catalysts (Wang *et al.*, 2009; Guan *et al.*, 2008). Therefore, in order to resolve these drawbacks, heterogeneous metalloporphyrin catalysts can be developed as a promising new catalytic system for selective oxidation of TMP.

At present, metalloporphyrins which can act as homogeneous catalysts to mimic the reactions of the cytochrome P-450 enzymes have aroused great attention in the literature. These compounds are able to catalyze several reactions of organic and inorganic substrates including styrene, cyclohexene, *N,N*-dimethylaniline, cyclohexane, *n*-hexane and benzyl alcohol under mild conditions (Omagari *et al.*, 2016; Sakthipriya and Ananthi, 2016; Agarwal and Bhat, 2016; Da Silva *et al.*, 2017; Wang *et al.*, 2016; Rahimi *et al.*, 2011; Ren *et al.*, 2010). While homogeneous catalytic systems provide high product yields, metalloporphyrins have the tendency to quickly degrade their ligands due to the self-aggregation by π - π stacking interactions (Nakagaki *et al.*, 2014; Adam and Ooi, 2012; Guo *et al.*, 2011). Likewise, the introduction of electron-withdrawing substituents such as the sulfonatophenyl group in the *meso*-position of metalloporphyrins generally helps to improve their stability and enhance the catalytic efficiency (Castro *et al.*, 2017; Tabor *et al.*, 2016; Feng *et al.*, 2015). Consequently, a synthetic approach based on the electrostatic binding of ionic metalloporphyrin molecules to positively charged imidazolium-based ILs is presented in the current study by using anionic metalloporphyrin complexes of *meso*-tetra-(4-sulfonatophenyl)porphyrin (MTSPP) and the functionalized imidazolium cationic-based ILs of 1-(3-triethoxysilylpropyl)-3-methylimidazolium chloride salt. The proposed immobilization of IL on the mesoporous silica SBA-15 support is as shown schematically in Figure 1.1.



Figures 1.1 Immobilization of MTSPP complexes on ionic liquid-functionalized SBA-15

Immobilization of metalloporphyrins onto functionalized imidazolium-based ILs represents a technique that combines the solvent properties of ILs with the robust nature of the solid support, and the biomimetic properties of the metalloporphyrin catalysts. In this approach, the ionic metalloporphyrin is introduced in the

imidazolium-based IL supported on mesoporous silica SBA-15 via electrostatic interaction. Therefore, the main role of the IL in the catalyst system is to improve the dispersion of the anionic metalloporphyrin molecules on the silica nanoparticles, while promoting the diffusion of reactants over the catalytic surface of the pores, and allowing for the reaction products to be released efficiently into the reaction medium. In the present study, immobilization of metalloporphyrins onto functionalized imidazolium-based ILs for the one-step oxidation of TMP is expected to facilitate the reactant access to the catalytic sites, prevent rapid catalyst deactivation, enhance catalyst stability as well as improve the yield of TMBQ. Most importantly, the SBA-15 supported ILs catalysts can be recycled and reused, which promotes green catalytic processes for the production of TMBQ.

1.3 Research Hypothesis

Based on the above problem statements, the following hypotheses have been formulated:

- i. Introduction of sulfonatophenyl groups as electron withdrawing substituents in the *meso*-position of supported metalloporphyrin complexes (MTSPP) can tune the energy level and have an effect on the electronic structure leading to superior performance of heterogenous catalysts.
- ii. Functionalized imidazolium cationic-based IL (ImIL) as a chemical linker can greatly improve the dispersion and solubility of the MTSPP on silica support. The strong interactions between MTSPP and the ImIL@SBA-15 silica surface might induce a synergistic effect of improving the catalytic activity of MTSPP-ImIL@SBA-15.
- iii. Homogeneous MTSPP complex species leached from the support are insignificant and does not contribute to the overall catalytic activity.
- iv. Iron and manganese are known biomimetics of the heme enzymes, including cytochrome P-450. Anionic MTSPP species containing the first row transition metals consisting of Fe, Mn, Cu or Zn are

hypothesized to be the main catalyst for the formation of the main product in the oxidation of TMP.

1.4 Objectives of Study

The main objectives of the research are as follows:

- i. To synthesize anionic metalloporphyrin complexes of *meso*-tetra-(4-sulfonatophenyl)porphyrin (MTSPP).
- ii. To synthesize imidazolium cationic-based IL-functionalized onto mesoporous SBA-15 support (ImIL@SBA nanocomposites).
- iii. To immobilize MTSPP complexes on ImIL@SBA nanocomposites.
- iv. To characterize the physicochemical properties of the ImIL@SBA and MTSPP immobilized on ImIL@SBA nanocomposites.
- v. To optimize the catalytic activity of MTSPP immobilized on ImIL@SBA in the oxidation of TMP to produce TMBQ.

1.5 Scope of Study

The scopes of this research focused on the synthesis of free-base porphyrin, anionic *meso*-tetra-(4-sulfonatophenyl)porphyrin (H_2TSPP). Then, H_2TSPP was coordinated to the first row transition metals including Mn(II), Fe(II), Cu(II) and Zn(II). The physicochemical properties of prepared metalloporphyrin complexes (MTSPP) were characterized using FT-IR, 1H -NMR, UV-Vis spectroscopy and MALDI-TOF-MS spectrometry.

On the other hand, ImIL@SBA nanocomposites were synthesized via post-grafting method between imidazolium cationic-based IL of 1-(3-triethoxysilylpropyl)-3-methylimidazolium chloride salt, C_3mimCl (ImIL) and mesoporous silica SBA-15. The physicochemical properties of the ImIL@SBA nanocomposites were

characterized using FTIR, SAXS, nitrogen adsorption-desorption isotherm analysis, TGA, FESEM, TEM, ^{29}Si MAS NMR and ^{13}C CP-MAS NMR spectroscopy. Next, the prepared MTSPP complexes, was immobilized onto ImIL@SBA nanocomposite by post-synthesis ion-exchange method and the resulting organic-inorganic hybrid materials, MTSPP-ImIL@SBA were characterized using FTIR, nitrogen adsorption-desorption isotherm analysis, SAXS, DR UV-Vis spectroscopy, TGA, FESEM, EDX, TEM and ICP-OES spectrometry.

Finally, the catalytic performances of the prepared MTSPP-ImIL@SBA were tested in the oxidation of TMP. The catalytic oxidation reaction was monitored by using GC-FID and GC-MS. Oxidation of TMP over blank reactions have also been carried out by using MTSPP complexes, imidazolium cationic-based IL (C_3mimCl), SBA-15, and without catalyst for the comparison. Reusability, leaching test, effect of reaction parameters (temperature, time, solvent and catalyst loading) and reaction mechanism were also studied.

1.6 Outline of Study

Figure 1.2 represents the outline for this research which includes the synthesis, characterizations and application of immobilized MTSPP complexes onto ImIL@SBA nanocomposite in the catalytic oxidation of TMP.

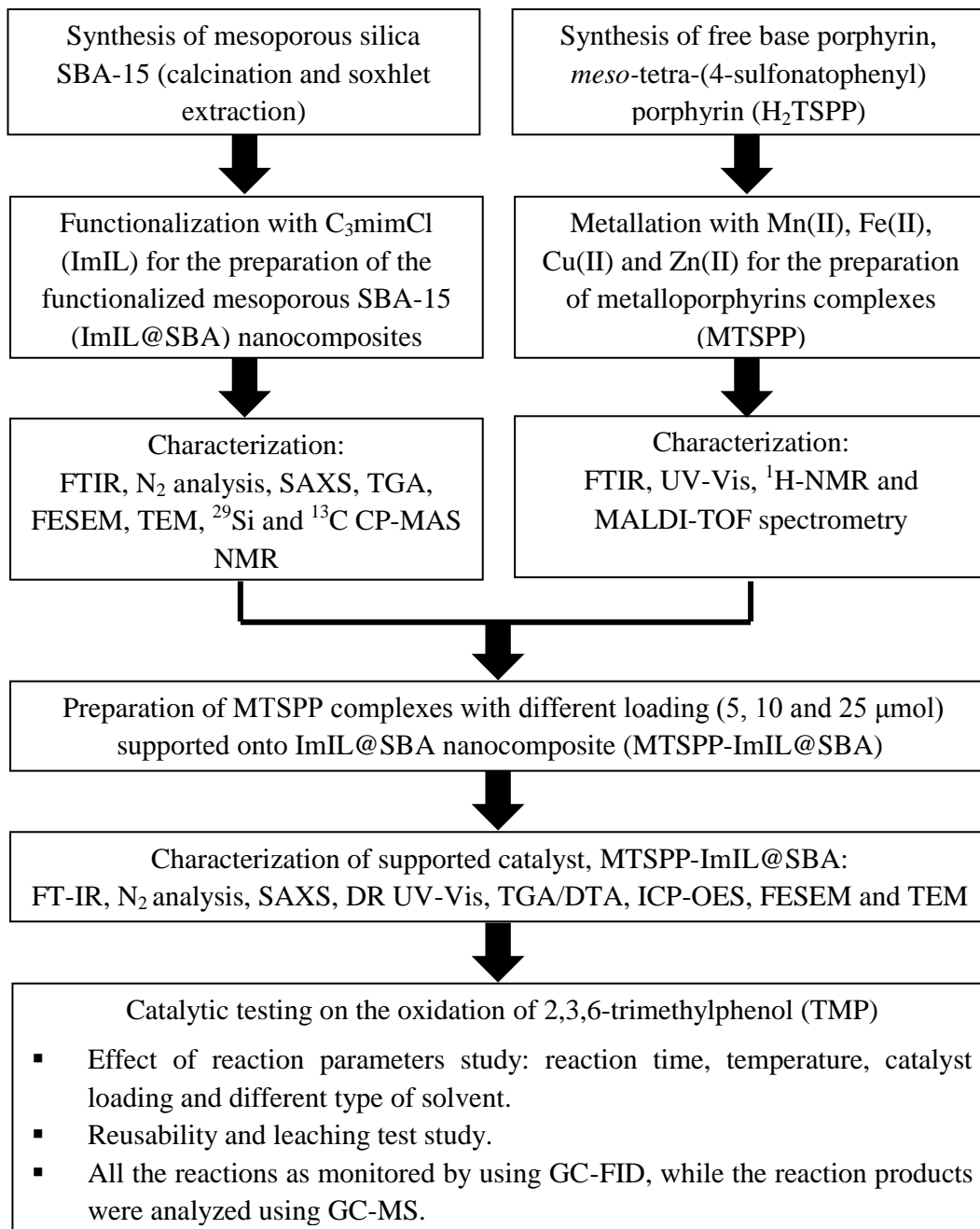


Figure 1.2 Outline of study

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